

**Semi-empirical correction of *ab initio* harmonic properties
by scaling factors: a validated uncertainty model
for calibration and prediction**

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Bayesian Model Calibration is used to revisit the problem of scaling factor calibration for semi-empirical correction of *ab initio* harmonic properties (*e.g.* vibrational frequencies and zero-point energies). A particular attention is devoted to the evaluation of scaling factor uncertainty, and to its effect on the accuracy of scaled properties. We argue that in most cases of interest the standard calibration model is not statistically valid, in the sense that *it is not able to fit a set of experimental calibration data within their uncertainty limits*. This impairs any attempt to use the results of the standard model for uncertainty analysis and/or uncertainty propagation. We propose to include a stochastic term in the calibration model to account for model inadequacy. This new model is validated in the Bayesian Model Calibration framework. We provide explicit formulae for prediction uncertainty in typical limit cases: large and small calibration sets of data with negligible measurement uncertainty, and datasets with large measurement uncertainties.

Keywords: Bayesian data analysis; Model calibration; Uncertainty propagation; Scaling factor; Vibrational frequency; Zero point energy.

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I. INTRODUCTION

One considers generally two types of uncertainty, arising either from random errors or from systematic errors. In quantum computational chemistry, random uncertainties, such as those arising from non-zero convergence threshold, have been shown by Irikura *et al.*¹ to be negligible. The major uncertainty sources are *biases* due to basis-set and/or theory limitations. For quantum chemistry to be predictive, *i.e.* to be able to *predict observables with confidence intervals*, these biases have to be corrected. A common way to do this is by semi-empirical corrections, *i.e.* corrections by additive or multiplicative factors calibrated on sets of experimental data.^{2–6}

Semi-empirical corrections of *ab initio* results by linear scaling are efficient for many observables. It is often overlooked that semi-empirical corrections are statistical operations, and as such, accompanied by an uncertainty which has to be considered in the uncertainty budget of model predictions, of which it is liable to be a major contribution. A sound uncertainty budget for these corrections is important in many circumstances. For instance, it is acknowledged that ZPE is a major source of uncertainty in thermochemistry with chemical accuracy.^{7–9} A good evaluation of ZPE prediction uncertainty is therefore essential for the assessment of the accuracy of computed thermochemical properties. In another field, infrared spectral fingerprinting, confidence intervals on corrected vibrational frequencies could help to ascertain the identification of spectral features.^{10–16} Estimation of uncertainty on computational chemistry results is also of paramount importance for their transfer in multi-scale chemical modeling.^{17,18} As quantum computational chemistry is at the lowest scale of chemical simulation, uncertainty on its results has to be carefully propagated to the higher scales in order to get quantified predictions. An example is the use of computational thermochemistry to predict the rates of reactions that could have a direct impact on macroscopic observables in combustion simulations.¹⁹

The concept of *Virtual Measurement* has been introduced by Irikura *et al.*,¹ with the aim to recast model outputs in the standardized uncertainty management framework established for experimental measurements in the *Guide to the Expression of Uncertainty in Measurement* (also known as "the GUM").²⁰ To be a Virtual Measurement, a model output has to be qualified by a standard uncertainty or confidence interval.

In a recent article (hereafter IJKK09), Irikura *et al.*²¹ address the problem of uncertainty

evaluation for scaled zero-point energies (ZPE), in the continuity of their 2005 paper (hereafter IJK05) on vibrational frequencies.²² Scaling of harmonic vibrational frequencies²³ is an important example of semi-empirical correction method in computational chemistry, where estimation of a vibrational frequency ν is obtained by multiplying the corresponding harmonic vibrational frequency ω , routinely calculated by computational chemistry codes, by an empirical scaling factor s (Fig. 1)

$$\nu = \omega s. \quad (1)$$

Optimal scaling factors have been computed for numerous sets of theory/basis-set combinations.²⁴⁻²⁷

More sophisticated scaling schemes have been designed to increase the precision of semi-empirical corrections. They make use of frequency-range or mode adapted scaling factors for frequencies,^{13,26} or internal coordinate adapted scaling factors for force constants.²⁸⁻³⁰ In all cases, the scaling factors are optimized to reproduce at best a set of experimental data, and are affected by a calibration uncertainty, which depends on a few factors, as the size of the calibration set and the precision of the data within. We focus in the following on the importance of this calibration uncertainty and concentrate on the widely used uniform scaling factors (*i.e.* a single scaling factor for all frequencies), without loss of generality.

In the majority of publications about scaling factors, two summary statistics are provided for each theory/basis-set combination: the optimal scaling factor and the root mean squares deviation, characterizing the average distance between experimental and corrected values estimated on the calibration dataset. From a reference dataset of experimental $\{\nu_{exp,i}\}_{i=1}^N$ and calculated $\{\omega_i\}_{i=1}^N$ vibrational frequencies, the optimal scaling factor obtained by the least-squares procedure is

$$\hat{s} = \sum \omega_i \nu_{exp,i} / \sum \omega_i^2 \quad (2)$$

and the quality of the correction is estimated by the root mean squares (rms) value

$$\gamma = \left(\frac{1}{N} \sum (\nu_{exp,i} - \hat{s} \omega_i)^2 \right)^{1/2}. \quad (3)$$

To our knowledge, these values have not been explicitly used for uncertainty propagation, but the rms γ provides an estimate of the residual uncertainty resulting from the scaling correction ("something like the target accuracy",³¹ or "a surrogate for uncertainty" according to Irikura *et al.*²²), and is used as a criterion for theory/basis-set selection.

Acknowledging that scaling factors obtained by calibration on experimental datasets are uncertain, Irikura *et al.*^{21,22} proposed that (i) this uncertainty is the major contribution to

prediction uncertainty using the scaling model; and (ii) prediction uncertainty is proportional to the calculated harmonic property (frequency or ZPE). These authors argue also that scaling factors are accurate to only two significant figures, and that all other studies overstate their precision by reporting them with four figures. This approach has been adopted by the National Institute of Standards and Technology (NIST) and put into practice in the Computational Chemistry Comparison and Benchmark DataBase (CCCBDB),²⁷ section XIII.C.2, where scaling factors are provided with uncertainties derived according to the procedure of IJK05/IJKK09. These results can also have a direct impact on the criteria to define the best basis/method level of theory for a given observable.

In the present paper, we revisit the problem of scaling factor calibration and properties prediction through the Bayesian Model Calibration framework, reputed for providing consistent uncertainty evaluation and propagation.^{32–34} Section II presents the methodological elements used for calibration and validation procedures, which are applied to a few representative vibrational frequency and zero point vibrational energy datasets and compared to the approach by IJK05/IJKK09 in Section III. We point out a statistical inconsistency in this approach, the main consequence being a much too large scaling factor uncertainty, from which misleading conclusions can be derived. A set of recommendations for reliable uncertainty estimation of scaled properties is provided in the Conclusion. Bayesian calculations used in this study are fairly standard and straightforward, but for the sake of completeness and for readers unfamiliar with statistical modeling, detailed derivations are provided in the Appendix.

II. METHODS

In the following sections, we present the calibration procedure for uniform scaling factors of vibrational frequencies, but it can be easily transposed to any other property usually computed at the harmonic level and corrected by a multiplicative scaling factor (ZPE, entropy...). It is also straightforward to transpose this procedure to semi-empirical correction schemes involving multiple frequency-adapted scaling factors.

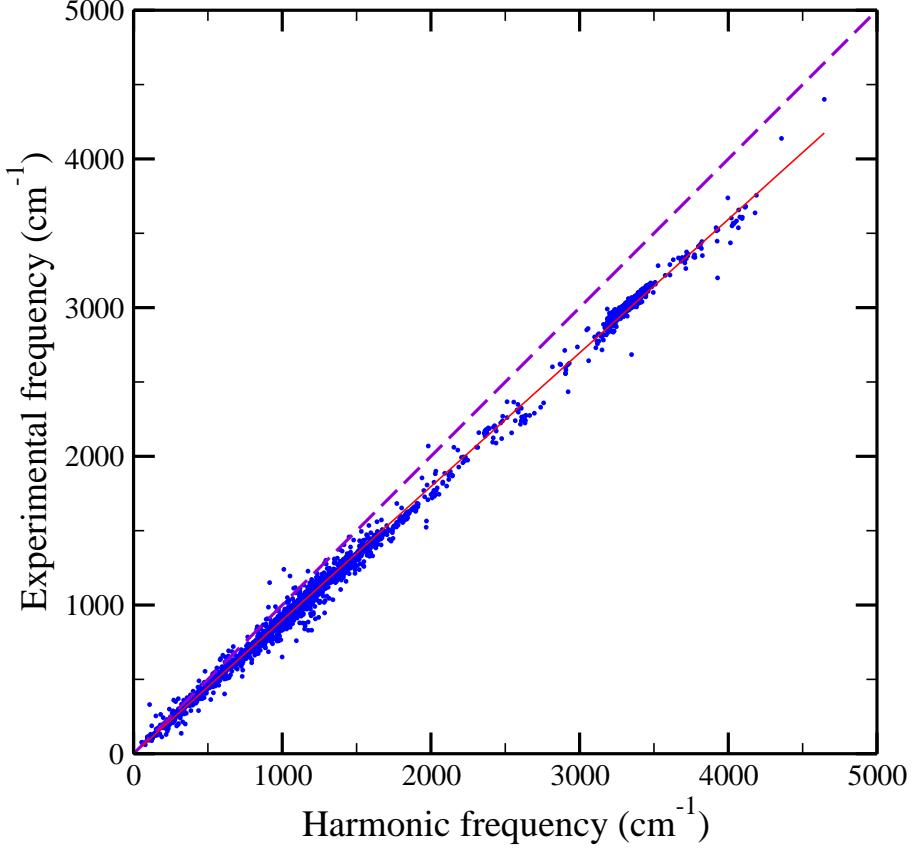


Figure 1. Correlation plot between calculated harmonic frequencies ω_i and measured frequencies ν_i^{exp} for a set of vibrations extracted from the CCCBDB for the HF/6-31G* combination of theory/basis-set (dots). The full line is the regression line $\nu_{exp} = s\omega$; the dashed line is a visual aid to appreciate the bias.

A. Scaling factor calibration

Considering a measured frequency ν_{exp} , one can assume that it is related to the true or exact value ν_{true} by

$$\nu_{exp} = \nu_{true} + \epsilon_{exp} \quad (4)$$

where $\epsilon_{exp} \sim N(0, u_{exp}^2)$ is a normal random variable, centered at zero with standard uncertainty u_{exp} , which represents the measurement error.

Calculated harmonic vibrational frequencies ω are also affected by random errors, related to numerical convergence defined by non-zero thresholds and the choice of starting point in geometry optimization, and to non-zero thresholds in wave-function optimization.¹ It has been shown that these uncertainties are negligible when compared to the measurement

uncertainty u_{exp} .¹ In the following, one can thus assume that, for one choice of theory/basis-set, the harmonic vibrational frequencies are computed without significant uncertainty.

1. The standard calibration model

If one makes the hypothesis of a linear relationship between ν_{true} and ω , as popularized by Pople *et al.*,² the *standard calibration model* is

$$\nu_{exp,i} = s\omega_i + \epsilon_{exp,i}, \quad (5)$$

where one considers a set of $i = 1, N$ frequencies. For a single frequency, there is an optimal scaling parameter $s_i = \nu_{exp,i}/\omega_i$. As $\nu_{exp,i}$ is uncertain, with standard uncertainty $u_{exp,i}$, the value of s_i cannot be known exactly and has a standard uncertainty $u_{s_i} = u_{exp,i}/\omega_i$. For a calibration dataset with uniform measurement uncertainty u_{exp} , it can be shown that the optimal value for s is given by the least squares solution \hat{s} , Eq. 2, and its standard uncertainty by $u_s = u_{exp}/\sqrt{\sum_{i=1}^N \omega_i^2}$ (*cf.* Section II C 3).

Applicability of this formula is subject to one condition: the model (Eq. 5) has to be statistically valid, which means that the residuals $\{\nu_{exp,i} - \hat{s}\omega_i\}_{i=1}^N$ should have a normal distribution centered on zero, with variance u_{exp}^2 . Normality is not always verified,²⁵ but most important, the variance condition is violated in most cases where precise data are used for calibration: the linear model (Eq. 5) is typically unable to reproduce a given set of measured frequencies *within their measurement uncertainty*. Consequently, the width of the distribution of residuals is dominated by model misfit instead of measurement uncertainty ($\gamma \gg u_{exp}$), which invalidates the distributional hypothesis of the standard calibration model (Eq. 5). In these conditions, this model *should not* be used to infer u_s , the uncertainty of s . Note that this is the key point to explain statistical inconsistencies in IJK05/IJKK09,^{21,22} as will be discussed later.

2. An improved calibration model

An option to solve this problem would be to search for better *ab initio* methods, able to reproduce experimental properties within their measurement uncertainties. This is an active research area which is out of the scope of the present study^{15,35–39}. Considering the practical

interest of correction by scaling factors, we rather focus on restoring statistical consistency by improving the calibration model.

Observing the apparent randomness of the residuals $\{\nu_{exp,i} - \hat{s}\omega_i\}_{i=1}^N$ (Fig. 2), we consider that the model misfit is not deterministically predictable. A solution to preserve a statistically valid linear scaling model is to introduce an additional stochastic variable ϵ_{mod} to represent the discrepancy between model and observations

$$\nu_{exp,i} = s\omega_i + \epsilon_{mod} + \epsilon_{exp,i}. \quad (6)$$

This equation is similar to the basic statistical model introduced by Kennedy and O'Hagan³² for Bayesian Calibration of Model Outputs. The discrepancy variable ϵ_{mod} could formally depend on ω , but we observed on representative datasets that the residuals between modeled and observed frequencies are not markedly frequency dependent (Fig. 2).⁴⁰ Therefore ϵ_{mod} is considered null in average, with unknown variance u_{mod}^2 :

$$\epsilon_{mod} \sim N(0, u_{mod}^2). \quad (7)$$

The new calibration model (Eq. 6) depends on two unknown parameters, s and u_{mod} .⁴¹

B. Model predictions and uncertainty propagation

The new stochastic prediction model used within the calibration model (Eq. 6),

$$\nu = s\omega + \epsilon_{mod}, \quad (8)$$

is linear with respect to uncertain variables s and ϵ_{mod} , and one can use standard uncertainty propagation rules²⁰ to estimate the average value and variance of predicted frequencies:

$$\bar{\nu} = \bar{s}\omega \quad (9)$$

$$u_{\nu}^2 = \left(\frac{\partial \nu}{\partial s} \right)_{s=\bar{s}}^2 u_s^2 + \left(\frac{\partial \nu}{\partial \epsilon_{mod}} \right)_{\epsilon_{mod}=0}^2 u_{mod}^2 \quad (10)$$

$$= \omega^2 u_s^2 + u_{mod}^2, \quad (11)$$

where \bar{s} denotes the average value of the scaling factor, and u_s^2 its variance.

In order to provide evaluated predictions of vibrational frequencies, we need therefore to estimate \bar{s} , u_s^2 and u_{mod}^2 from a calibration dataset. This is done in the next section, using Bayesian Model Calibration.

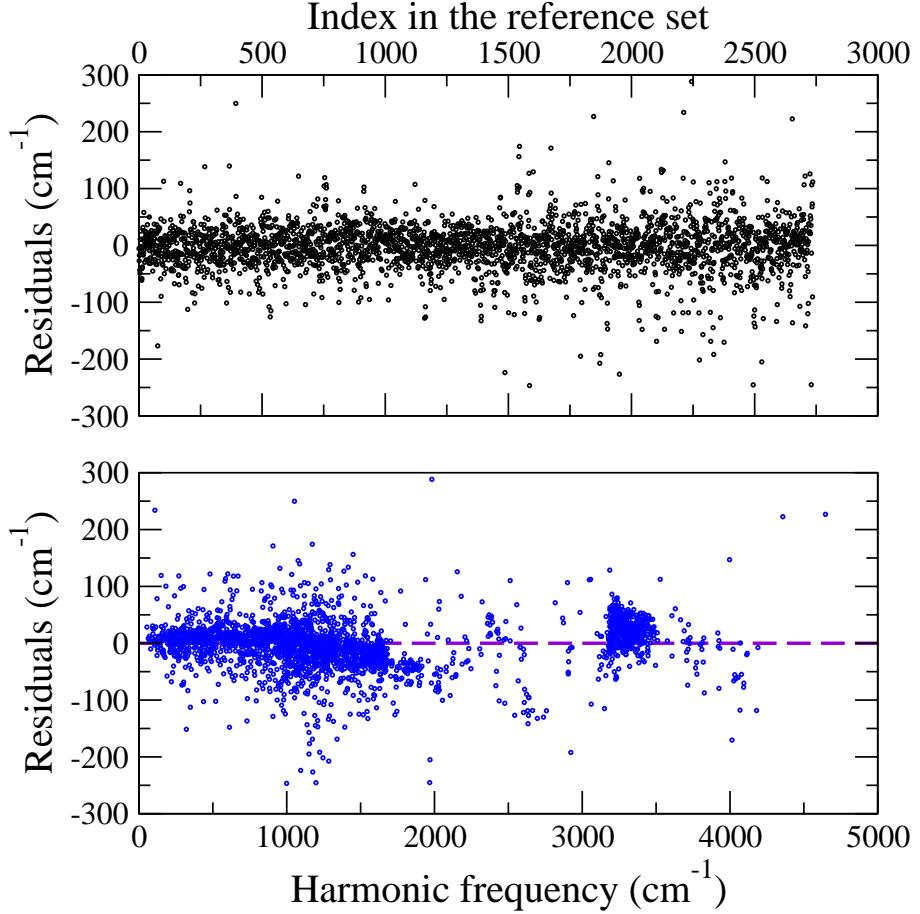


Figure 2. Residuals between calculated harmonic frequencies ω_i and measured frequencies ν_i for a set of vibrations extracted from the CCCBDB for the HF/6-31G* combination of theory/basis-set (dots). Bottom: residuals as a function of ω . In order to suppress the grouping effect linked with frequencies, the residuals were also plotted as a function of their order in the reference set (top).

C. Bayesian Model Calibration (BMC)

1. General case

Starting from the calibration model (Eq. 6), one derives the expression for the *posterior* probability density function (pdf) of the parameters, given a set of N measured and

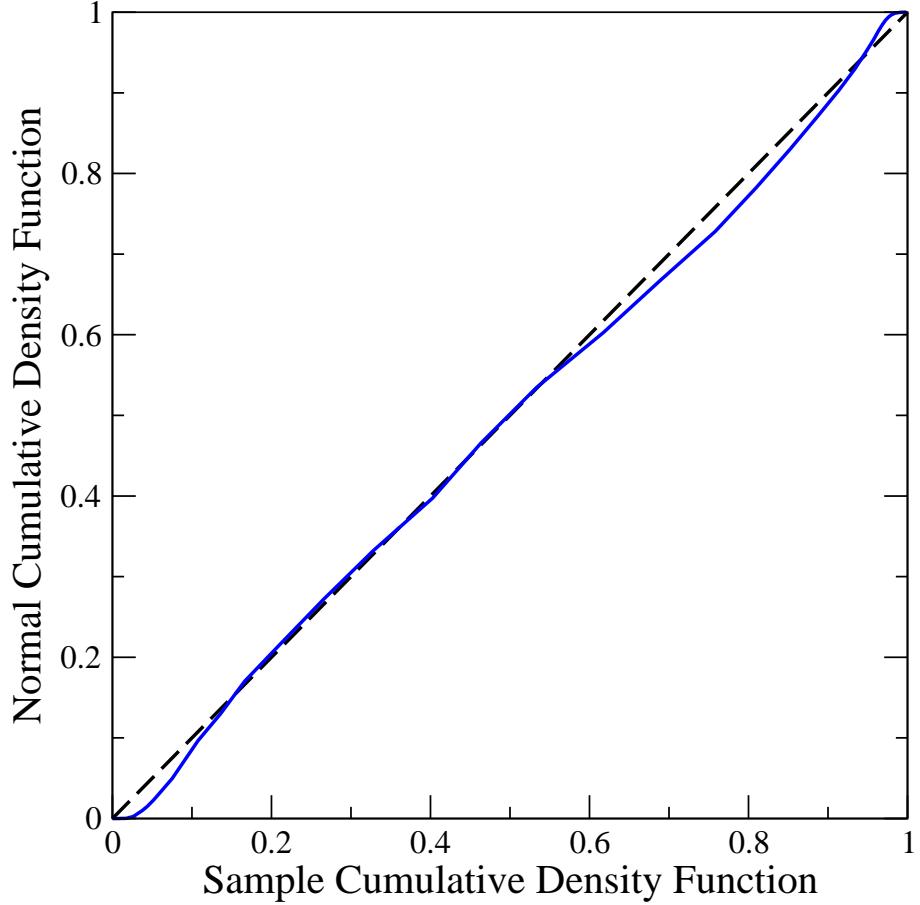


Figure 3. Plot of the cumulative density function (CDF) for the residuals (same as in Fig. 2) against a normal CDF shows that globally there is very little deviation from normality in this dataset.

calculated frequencies (details of derivation are provided in Appendix A 1)

$$p(s, u_{mod} | \{\nu_{exp,i}, u_{exp,i}, \omega_i\}_{i=1}^N) \propto \frac{1}{u_{mod} \prod_{i=1}^N \sqrt{u_{mod}^2 + u_{exp,i}^2}} \times \exp \left(- \sum_{i=1}^N \frac{(\nu_{exp,i} - s\omega_i)^2}{2(u_{mod}^2 + u_{exp,i}^2)} \right). \quad (12)$$

Estimates of \bar{s} , u_s^2 and u_{mod}^2 are obtained from this pdf. In the general case, this has to be done numerically.³³ Two limit cases of interest (*i.e.* negligible and very large measurement uncertainties), amenable to analytical results, are presented in the next sections.

2. The case of negligible measurement uncertainties

In the commonly met situation where the amplitude of the discrepancy between calibration model and experimental data is much larger than any other sources of uncertainty ($u_{mod} \gg u_{exp}$), we can consider the approximate calibration model

$$\nu_{exp,i} = s\omega_i + \epsilon_{mod}, \quad (13)$$

for which the posterior pdf (Eq. 12) can be simplified and rearranged to (see Appendix A 2)

$$p(s, u_{mod} | \{\nu_{exp,i}, \omega_i\}_{i=1}^N) \propto \frac{1}{u_{mod}^{N+1}} \exp\left(-\frac{N\gamma^2}{2u_{mod}^2}\right) \exp\left(-\frac{(s - \hat{s})^2 \sum_{i=1}^N \omega_i^2}{2u_{mod}^2}\right), \quad (14)$$

from which one can analytically derive estimates of the parameters:

- $\bar{s} = \hat{s}$: the average value for s is identical to the optimal value of least-squares analysis (Eq. 2);
- u_s , the standard uncertainty on s , is related to the rms γ by

$$u_s = \gamma \sqrt{N / \left[(N - 3) \sum \omega_i^2 \right]}; \quad (15)$$

- and the estimate of u_{mod}^2 is related to γ according to

$$\overline{u_{mod}^2} = \gamma^2 N / (N - 3). \quad (16)$$

Inserting these values in Eq. 11, we obtain the standard uncertainty of a predicted frequency:

$$u_\nu = \gamma \sqrt{\frac{N}{N - 3} \left(\frac{\omega^2}{\sum_i \omega_i^2} + 1 \right)}. \quad (17)$$

It can be seen that for large calibration sets of few hundreds of frequencies $\sqrt{N/(N - 3)} \simeq 1$ and $\omega^2 / \sum_i \omega_i^2 \ll 1$, and thus

$$u_\nu \simeq \gamma. \quad (18)$$

In such conditions, it is possible to derive directly confidence intervals on scaled properties from the summary calibration statistics \hat{s} and γ typically provided in the literature.^{24–26} Assuming the normality of uncertainty distributions, confidence intervals can be defined for prediction purpose, *e.g.* the 95% confidence interval for ν is given by

$$CI_{95}(\nu) = [\hat{s}\omega - 1.96 u_\nu, \hat{s}\omega + 1.96 u_\nu]. \quad (19)$$

3. The case of very large measurement uncertainties

When model discrepancy is negligible compared to measurement uncertainties ($u_{mod} \ll u_{exp}$), the standard linear model is statistically valid, and one recovers the Bayesian version of weighted least squares. The posterior pdf for s is then

$$p(s | \{\nu_{exp,i}, u_{exp,i}, \omega_i\}_{i=1}^N) \propto \prod_{i=1}^N u_{exp,i}^{-1} \exp\left(-\frac{1}{2} \sum_{i=1}^N \frac{(\nu_{exp,i} - s\omega_i)^2}{u_{exp,i}^2}\right), \quad (20)$$

from which one obtains

$$\hat{s} = \sum_{i=1}^N (\omega_i \nu_{exp,i} / u_{exp,i}^2) / \sum_{i=1}^N (\omega_i^2 / u_{exp,i}^2), \quad (21)$$

$$u_s^2 = 1 / \sum_{i=1}^N (\omega_i^2 / u_{exp,i}^2). \quad (22)$$

For uniform experimental uncertainty over the dataset, the scaling factor uncertainty is

$$u_s = u_{exp} / \sqrt{\sum_{i=1}^N \omega_i^2}. \quad (23)$$

D. The Multiplicative Uncertainty (MU) method

Irikura *et al.*²², after a thorough analysis of the uncertainty sources in the *ab initio* calculation of harmonic vibrational frequencies, proposed that the major contribution to prediction uncertainty would be the uncertainty on the scaling factor \hat{s} . They estimate u_s from the weighted variance of s with weights $a_i = \omega_i^2$. This weighting scheme is derived in two steps: (1) they propose that the probability density function (pdf) for the scaling factor is a linear combination of pdf's for individual scaling factors in the reference set; and (2) from the comparison of the expression of the average value derived from this proposition with the least-squares solution Eq. 2. This way, they obtain a standard uncertainty

$$u_s^* \simeq \left(\frac{1}{\sum \omega_i^2} \sum \omega_i^2 (s_i - \hat{s})^2 \right)^{1/2}, \quad (24)$$

which can be related to the rms γ by $u_s^* \simeq \gamma \sqrt{N / \sum \omega_i^2}$.

More recently, Irikura *et al.*²¹ derived another expression by standard uncertainty propagation from the least-squares solution Eq. 2, adding a new term to their previous expression

$$u_s^* \simeq \left(\frac{1}{\sum \omega_i^2} \sum \omega_i^2 (s_i - \hat{s})^2 + \frac{1}{(\sum \omega_i^2)^2} \sum \omega_i^2 u_{exp,i}^2 \right)^{1/2}. \quad (25)$$

They showed that the contribution of the latter term is negligible, validating the use of their former expression. Note that, unless all frequencies ω_i are equal, this uncertainty u_s^* is different from the dispersion of s values within the calibration set

$$\delta_s = \left(\frac{1}{N} \sum (s_i - \hat{s})^2 \right)^{1/2} \quad (26)$$

and attributes larger weights to the high frequencies.

Using either of Irikura *et al.*^{21,22} expressions for u_s^* , uncertainty on a scaled frequency is approximated by

$$u_\nu \simeq \omega u_s^*, \quad (27)$$

hence the name of "Multiplicative Uncertainty" (MU) used hereafter.

The salient feature of Eq. 27 is that prediction uncertainty is always proportional to the calculated harmonic frequency, ignoring the additive term present in Eq. 11. Simple statistical validation test of the MU method have apparently not been published and are performed in the next sections.

III. APPLICATIONS AND DISCUSSION

In the following, we validate the BMC approach and compare it to the MU approach on representative test cases of vibrational frequencies and zero point energies.

A. Vibrational frequencies

The reference dataset of 2737 frequencies for the HF/6-31G* combination of theory/basis-set has been downloaded from the NIST/CCCBDB in July 2008.²⁷ Correlation between experimental and harmonic frequencies is plotted in Fig. 1.

1. Calibration

In absence of detailed information on the measurement uncertainties for this dataset, and considering the typical high accuracy of spectroscopic data, we assume that they are negligible and apply the corresponding equations for the BMC model. Using Eqs. 15 and 16, we obtain $\hat{s} = 0.89843 \pm 0.00046$, and $u_{mod} = 45.35 \pm 0.61 \text{ cm}^{-1}$ (Table I). The latter

	Summary stat.		MU		BMC		
	\hat{s}	$\gamma(\text{cm}^{-1})$	u_s^*	%CI ₉₅	u_s	$u_{mod}(\text{cm}^{-1})$	%CI ₉₅
All frequencies ($N = 2737$)							
Full set	0.89843	45.33	0.025	-	0.00046	45.35	-
Calibration set	0.89860	45.27	0.024	-	0.00065	45.31	-
Validation set	-	-	-	83.0	-	-	94.6
High frequencies, between 3180 and 3500 cm⁻¹ ($N = 479$)							
Full set	0.90502	28.71	0.00869	-	0.00040	28.78	-
Calibration set	0.90517	23.32	0.01005	-	0.00046	23.44	-
Validation set	-	-	-	97.4	-	-	95.4

Table I. Statistical estimates and validation for MU and BMC models for vibrational frequencies extracted from the CCCBDB for the HF/6-31G* combination of theory/basis-set.

value is very close to the rms value $\gamma = 45.33 \text{ cm}^{-1}$, which validates the use of Eq. 18 for large calibration datasets.

For this same dataset, the CCCBDB proposes $\hat{s} = 0.899 \pm 0.025$, which can be recovered using Eq. 24 (Table I). The standard uncertainties on \hat{s} evaluated by both methods differ thus by a factor 50, which can be expected to have noticeable effect on prediction uncertainty (see Section III A 5). In order to visualize the difference, we plotted the 95 % confidence intervals on predicted frequencies obtained from both methods (Fig. 4). It is immediately visible that the the MU approach has a tendency to underestimate uncertainty at low frequencies and to overestimate it at high frequencies.

2. Validation

To better quantify this inconsistency, we performed a standard test in statistical calibration/prediction: the dataset is split randomly in two subsets, one for calibration, the other one for validation. Both sets are taken here of equal size (plus or minus one unit). In this case, one gets slightly different values of the parameters, as reported in Table I. Using these values, we generate 95 % confidence intervals (Eq. 19; the residuals of this dataset have a nearly normal distribution) and calculate the percentage of inclusion of the exper-

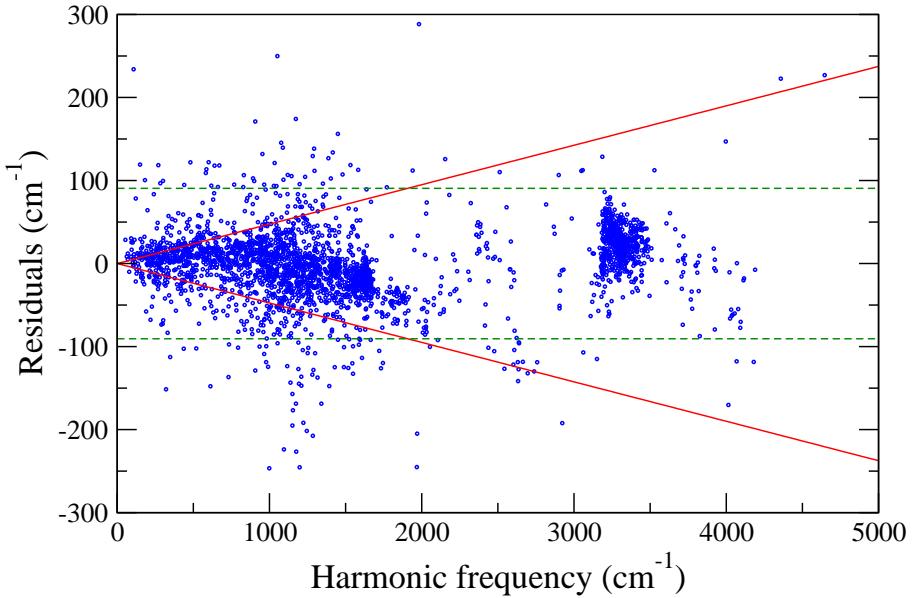


Figure 4. Residuals of the linear scaling model for a set of 2737 vibrational frequencies and the HF/6-31G* combination of theory/basis-set (dots). Model 95 % confidence intervals for residuals: dashed (green) lines for the Bayesian Model Calibration method; solid (red) lines for the Multiplicative Uncertainty model of IJK05/IJKK09.

imental values of the validation subset within these prediction intervals (Fig. 4). For a consistent predictor, one should find a frequency close to 95 %. BMC succeeds for 94.7 % of the frequencies in the validation set, whereas the MU model succeeds for only 83 % (Table I). Considering the size of the samples, the difference is significant, and the statistical consistency of the MU approach can be questioned. When contrasted with the BMC, one understands that the MU method, which does not consider model inadequacy explicitly, "absorbs" it at least partially in u_s^* .

3. *Test on a restricted frequency scale*

As stated in IJK05, "to apply the fractional bias correction, it is important to select a class of frequencies similar to the ones to be estimated".²² For instance, if one selects in the reference set only those frequencies between 3180 and 3500 cm^{-1} , one gets a much more uniform picture than with the full reference set.

The MU calibration procedure was done with this limited set of 479 frequencies, providing $\hat{s} = 0.9050 \pm 0.0087$ (Table I). In this case, the uncertainty factor for s is practically identical

to the standard deviation calculated from the sample (0.00869 vs. 0.00871): $u_s^* \simeq \delta_s$. Due to the restricted frequency range, one has indeed $\omega_i^2 / \sum_i \omega_i^2 \simeq 1/N$, hence the identity between evaluations by Eqs 24 and 26.

This set has been split in two, as before. The scaling factor obtained by MU from the calibration subset is now $\hat{s} = 0.9052 \pm 0.0071$, and 97.4 % of the validation frequencies fall within the 95 % confidence interval. This result is quite close to the one obtained with BMC (Table I).

It appears thus that in restrictive conditions, the MU method can be valid for reference sets where the individual scaling factors are uniformly distributed with regard to the harmonic frequencies. In such cases however, the uncertainty is recovered as the conventional unweighted standard deviation of the sample of individual scaling factors (Eq. 26). Note also that the MU method is used in the CCCBDB out of these favorable conditions.²⁷

4. *Significant figures and uncertainty reporting*

Good practice in uncertainty reporting is to provide one or two significant figures for the uncertainty and to truncate the average/optimal value at the same level.²⁰ If the reported number is to be used in further calculations (which is the case for uncertainty propagation), two digits is better. The common practice is to publish scaling factors for vibrational frequencies with four significant digits.^{24–26} At the risk of being pedantic, one could argue that they should be reported with *five* significant digits, e.g. $\hat{s} = 0.89843 \pm 0.00046$, in sharp contrast with the two digits recommendation of Irikura *et al.*,²² based on their biased scaling factor uncertainty evaluation.

5. *Prediction and uncertainty propagation*

The relative importance of both factors u_s^2 and u_{mod}^2 in Eq. 11 can be evaluated on the example of a calculated harmonic frequency in the higher frequency range $\omega = 3000 \text{ cm}^{-1}$ (Table II).

In this case, the uncertainty on the scaling factor contributes only to one thousandth of the total prediction variance. When dealing with large datasets of accurate vibrational frequencies, the uncertainty on the scaling factor can thus be neglected. The uncertainty

Property	Theory/Basis set	ω	Method	$\omega^2 u_s^2$	u_{mod}^2	$\nu \pm u_\nu$
Frequency	HF/6-31G*	3000 cm ⁻¹	BMC	2.25	2052.09	2695±45 cm ⁻¹
			MU	5625.0	-	2695±75 cm ⁻¹
ZPE	HF/6-31G*	100 kJ mol ⁻¹	BMC	0.073	0.53	91.35±0.78 kJ mol ⁻¹
			MU	2.592	-	91.35±1.61 kJ mol ⁻¹
ZPE	B3LYP/6-31G*	100 kJ mol ⁻¹	BMC	0.029	0.19	98.12±0.47 kJ mol ⁻¹
			MU	1.061	-	98.12±1.03 kJ mol ⁻¹

Table II. Compared prediction uncertainty with the BMC and MU methods for a set of 2737 vibrational frequencies extracted from the CCCBDB for the HF/6-31G* combination of theory/basis-set and for a set of 39 ZPE of the Z1 set for the HF/6-31G* and B3LYP/6-31G* combinations.

on u_{mod} is also much too small to be relevant for confidence intervals calculation. One can therefore safely apply the uncertainty propagation formula (Eq. 18), using the rms provided by most reference articles dealing with scaling factors calibration.^{24–26} For smaller calibration sets, the rms can be seen as an inferior limit to prediction uncertainty, and Eq. 17 would provide more reliable confidence intervals (see next Section).

Comparing the prediction uncertainties for the BMC (45 cm⁻¹) and MU (75 cm⁻¹) methods, one sees that the factor 50 between u_s and u_s^* observed at the calibration stage is partially damped at the prediction level by the fact that the BMC uncertainty is strongly dominated by the model inadequacy parameter u_{mod} .

B. Zero Point Vibrational Energies

We consider ZPE as an additional test because the reference datasets are considerably smaller than for the vibrational frequencies (e.g. 39 molecules in the Z1 set of Merrick *et al.*²⁶), which is expected to emphasize the role of u_s , the uncertainty on the scaling factor. The uncertainties reported by Irikura⁴² for diatomic molecules are typically very small (on the order of 0.01 cm⁻¹), but transposition to larger molecules is not straightforward. In the absence of a systematic review of measurement errors for ZPE of polyatomic molecules, we consider here that they can be neglected. The effect of non-negligible measurement

uncertainties is addressed at the end of this section.

1. Calibration - Validation

Using BMC with the Z1 reference set, one gets $\hat{s} = 0.9135 \pm 0.0027$ and $u_{mod} = 0.731 \pm 0.086 \text{ kJ mol}^{-1}$ (Table III), which is consistent with the rms obtained by Merrick *et al.*²⁶ for the HF/6-31G* theory/basis-set combination. Relative uncertainties on these parameters have been increased by one order of magnitude, when compared to the vibrational frequencies case, a direct effect of the smaller sample size. The validation test shows once more that the MU model fails to provide correct confidence intervals, with a score of only 0.63 for CI_{95} (Table III).

2. Uncertainty propagation

For such a small reference dataset, it is interesting to check if the approximate formula (Eq. 18) for uncertainty propagation, which was validated for large sets of vibrational frequencies still holds, *i.e.* if the contribution of the multiplicative term involving u_s stays negligible or not for the larger ZPE values. If one considers a calculated ZPE of 100 kJ mol⁻¹ (HF/6-31G*), one has $u_\nu = \sqrt{(100 * 0.0027)^2 + 0.73^2} = 0.78 \text{ kJ mol}^{-1}$, to be compared to $\gamma = 0.71 \text{ kJ mol}^{-1}$ (Table III). It is to be noted also that the uncertainty on u_{mod} might also contribute, with $u_{u_{mod}} = 0.09 \text{ kJ mol}^{-1}$. Taking all uncertainty sources into account through Eq. A27 by Monte Carlo Uncertainty Propagation (MCUP),³⁴ one gets $u_\nu = 0.77 \text{ kJ mol}^{-1}$. The uncertainty on u_{mod} can therefore be neglected.

In the same conditions, for the combination B3LYP/6-31G*, one gets $\gamma = 0.42 \text{ kJ mol}^{-1}$ and $u_\nu = 0.47 \text{ kJ mol}^{-1}$, to be compared with a reference value obtained by MCUP of $u_\nu = 0.47 \text{ kJ mol}^{-1}$ (Table III).

There is globally only a 10% increase compared to the rms γ . In this range of ZPEs, γ still provides a good approximation of the prediction uncertainty (Table II). However, the amplitude of the discrepancy between γ and u_ν will probably increase with the size of the molecule. In consequence, for uncertainty propagation with ZPEs, notably for large molecules, it would be safer to use the full UP formula (Eq. 17), involving the multiplicative uncertainty factor. Compilations of scaling factors for ZPE should thus report the easily

	Summary stat.		MU			BMC	
	\hat{s}	$\gamma(\text{kJ mol}^{-1})$	u_s^*	%CI ₉₅	u_s	$u_{mod}(\text{kJ mol}^{-1})$	%CI ₉₅
HF/6-31G*							
Full set	0.9135	0.707	0.0161	-	0.0027	0.731 ± 0.086	-
Calibration set	0.9078	0.773	0.0214		0.0052	0.826 ± 0.143	
Validation set				0.63			0.95
B3LYP/6-31G*							
Full set	0.9812	0.423	0.0103	-	0.0017	0.437 ± 0.052	-
Calibration set	0.9825	0.448	0.0134		0.0032	0.478 ± 0.083	
Validation set				0.63			1.00

Table III. Statistical estimates and validation for MU and BMC models for a set of 39 ZPVEs of the Z1 set for the HF/6-31G* and B2LYP/6-31G* combinations of theory/basis-set.

calculated value of $u_s = \gamma \sqrt{N / ((N - 3) \sum \omega_i^2)}$, in addition to the rms γ .

3. The case of non-negligible experimental uncertainties

When the measurement uncertainty becomes comparable to the rms, model inadequacy should be small, and confidence intervals for prediction should account for the measurement uncertainty (Eq. 11). In the absence of an exhaustive compilation of experimental uncertainties on measured ZPE, we performed simulations assuming a uniform uncertainty distribution over the full dataset. In order to test the sensitivity of the model parameters to this uncertainty, we repeated the estimations of the previous section, using Eq. A6, for values of u_{exp} between 0.1 and 1.0 kJ mol^{-1} . The results are reported in Fig. 5.

As expected from the properties of the posterior pdf (Eq. 12), the average/optimal value of the scaling factor is not sensitive to the amplitude of u_{exp} . Moreover, we observe only a slight absolute increase of u_s from 0.002 to 0.004. A transition from a constant u_s , defined by the $u_{exp} = 0$ limit, to a linear increase consistent with the weighted least squares limit (Eq. 23) is observed around $u_{exp} = \gamma$, where both limit equations intersect. A closer look shows that the transition occurs indeed at values of u_{exp} slightly smaller than γ , in a region

($u_{exp} \simeq 0.35$) where u_s displays a minimum.

The evolution of the model inadequacy factor u_{mod} is more dramatic: it displays a sharp decrease and falls down to zero as soon as the measurement uncertainty reaches the value of the rms γ . For values of u_{exp} below 0.25, u_{mod} follows the $u_{mod}^2 + u_{exp}^2 = \gamma^2$ law (represented as a dashed line in Fig. 5), but the calculated decrease becomes much faster in the transition zone. The uncertainty on u_{mod} increases notably in the transition region.

In the limit of large experimental uncertainties, using Eq. 23, the uncertainty propagation formula can be written as

$$u_\nu^2 = \omega^2 u_s^2 = u_{exp}^2 \omega^2 / \sum \omega_i^2. \quad (28)$$

In this case, the model inadequacy variable ϵ_{mod} becomes useless, as the standard calibration model is statistically valid.

This test shows that the BMC model is able to adapt nicely to various conditions of measurement uncertainty, with an automatic and smooth transition from the "model inadequacy"- to the "measurement uncertainty"-dominated regimes.

IV. CONCLUSIONS AND RECOMMENDATIONS

A reanalysis of the scaling factor calibration problem as stated by Irikura *et al.*^{21,22} identified two uncertainty components, besides the experimental one: a parametric uncertainty u_s attached to the optimal scaling factor, and a model inadequacy factor u_{mod} accounting for the inability of the linear scaling correction model to reproduce sets of calibration data within their experimental uncertainties. A general estimation framework, based on Bayesian Model Calibration, has been defined and validated in cases of interest.

The general formula for prediction of a scaled property ν from a harmonic value ω is

$$\nu = \hat{s}\omega \pm u_\nu, \quad (29)$$

where \hat{s} is the optimal value of the scaling factor provided by the least squares formula (Eq. 2) for negligible or uniform measurement uncertainty, or more generally by the weighted least squares formula (Eq. 21), and u_ν is a standard uncertainty, for which explicit expressions have been derived in limit cases, depending on the size and precision of the calibration set:

- large calibration sets of precise data ($u_{exp} \ll \gamma$): $u_\nu(\omega) = \gamma$;

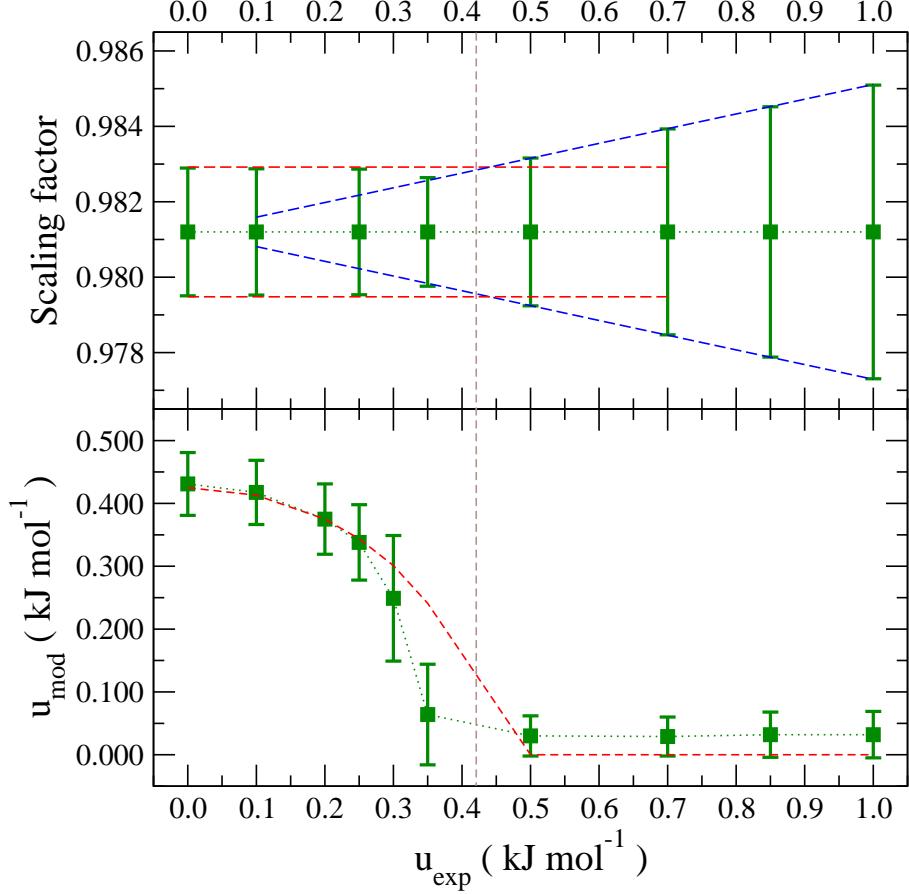


Figure 5. Evolution of measurement model parameters with the amplitude of an hypothetical uniform experimental measurement uncertainty u_{exp} on ZPE; B3LYP/6-31G* combination of theory/basis-set (green squares with error bars). The brown vertical dashed line indicates the value of the rms γ . Top panel: the red dashed lines represent the 1σ confidence interval in the limit of null experimental uncertainty; the blue dashed line represent the 1σ confidence interval in the weighted least squares limit. Bottom panel: the red dashed line represents the $u_{mod}^2 + u_{exp}^2 = \gamma^2$ law, truncated to positive values of u_{mod} .

- small calibration sets of precise data ($u_{exp} \ll \gamma$): $u_\nu(\omega) = \gamma \sqrt{\frac{N}{N-3} (1 + \omega^2 / \sum_i \omega_i^2)}$;
- calibration sets with large measurement uncertainties ($u_{exp} \geq \gamma$): $u_\nu(\omega) = \omega / \sqrt{\sum_i \omega_i^2 / u_{exp,i}^2}$ simplified to $u_\nu(\omega) = u_{exp} \omega / \sqrt{\sum_i \omega_i^2}$ for uniform measurement uncertainty.

The Multiplicative Uncertainty method proposed by Irikura *et al.*^{21,22} has been shown here to be statistically inconsistent when large frequency ranges are considered. It is only valid in particular situations, either when the dataset spans a restricted frequency range (in which

case the uncertainty is reduced to a trivial unweighted standard deviation), or in the extreme case of large uniform measurement uncertainty in the calibration dataset. For vibrational frequencies, the MU method underestimates prediction uncertainty for small values of ω and overestimate it (up to a factor 2) at the high end of the ω scale.

We would like to stress out that the validity of the formulas proposed above for uncertainty propagation depends to some extent on the normality of the residuals $\{\nu_i - \hat{s}\omega_i\}_{i=1}^N$ of the linear regression. Inspection of histograms of residuals (see *e.g.* Fig. 1 in Ref.²⁵) shows that this is not always the case. The usual approach of choosing an optimal theory/basis-set combination is to assess their performance by the rms alone, maybe weighted by computational cost considerations.^{24–26} Researchers concerned by prediction uncertainty might also consider an additional "normality criterion" in order to reject theory/basis-set combinations providing non-normal residuals and from which the summary statistics cannot be used reliably for uncertainty propagation. Analysis of restricted ranges of data as presently done by some authors for vibrational frequencies^{13,26} is one way to improve the normality of residuals, but as demonstrated above, prediction from small calibration sets calls for more information than the rms.

A. Recommendations to calibrators of scaling factors

1. For large calibration sets of accurate data, as the ones used for calibration of uniform scaling factors for vibrational frequencies, reliable prediction uncertainty can be simply based on the rms γ (Eq. 3). In this case, prediction uncertainty is purely additive.
2. For much smaller datasets of a few dozens of data or less, as in the case of ZPEs or mode-specific frequencies, one has a combination of additive and multiplicative uncertainty (or rather, variance). Ideally, uncertainty on the scaling factor $u_s = \gamma \sqrt{N/((N-3)\sum \omega_i^2)}$ should be reported along with the additive term $u_{mod} = \gamma \sqrt{N/(N-3)}$, for use in the general uncertainty propagation equation $u_\nu^2 = \omega^2 u_s^2 + u_{mod}^2$ (Eq. 11). It certainly would be a large step towards the general applicability of the Virtual Measurement concept,¹ if statistically pertinent estimators were systematically reported in the literature devoted to the calibration of semi-empirical correction parameters.

3. An indicator of the normality of the residuals in the calibration dataset would also be welcomed.

B. Recommendations to users of scaling factors

1. For the end user of scaling factors, it is important to remind, as pertinently stated by Irikura *et al.*^{21,22}, that semi-empirical correction of a property by scaling is not a deterministic procedure: a scaled property has an attached uncertainty, which depends on the level of theory/basis-set used for the calculation of harmonic properties (it depends also on the quantity and quality of the calibration dataset, but this is out of reach of the end user).
2. In the present state of affairs, the best estimate of the prediction uncertainty available for most levels of theory/basis-set is the rms γ , *i.e.* one has to assume $u_\nu \simeq \gamma$.^{24–26} The use of the multiplicative scaling factor uncertainty as reported presently (March 2010) in the CCCBDB²⁷ cannot be recommended for the estimation of uncertainty of scaled properties.
3. Users are encouraged to
 - (a) report the uncertainty along with the scaled properties, *i.e.* $\nu = \hat{s}\omega \pm u_\nu$, and
 - (b) account for uncertainty when scaled properties are used as inputs to a model^{20,34}, or for comparison with experimental data.
4. One has to be conscious that γ provides only a lower limit of the uncertainty for properties with small calibration data sets (*e.g.* ZPE). For numerical examples, see Table II.

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Appendix A: Appendix

1. Bayesian analysis of scaling factor calibration model

We consider the calibration model

$$\nu_{exp,i} = s\omega_i + \epsilon_{mod} + \epsilon_{exp,i}, \quad (A1)$$

where $\epsilon_{exp,i} \sim N(0, u_{exp,i}^2)$ is the measurement uncertainty of $\nu_{exp,i}$, and $\epsilon_{mod} \sim N(0, u_{mod}^2)$ is a variable accounting for the discrepancy between the linear model and the observations. This model has two unknown parameters, s and u_{mod} , to be estimated on a calibration dataset consisting of N calculated harmonic frequencies $\{\omega_i\}_{i=1}^N$, and their corresponding experimental frequencies $\{\nu_{exp,i}, u_{exp,i}\}_{i=1}^N$.

In the Bayesian data analysis framework,^{33,43} all information about parameters can be obtained from the joint posterior pdf $p(s, u_{mod} | \{\nu_{exp,i}, u_{exp,i}, \omega_i\}_{i=1}^N)$. In order to simplify the notations, we will omit in the following the list indices when they are not necessary. This pdf is obtained through Bayes theorem

$$p(s, u_{mod} | \{\nu_{exp}, u_{exp}, \omega\}) \propto p(\{\nu_{exp}\} | s, u_{mod}, \{u_{exp}, \omega\}) p(s, u_{mod}), \quad (A2)$$

where $p(\{\nu_{exp}\} | s, u_{mod}, \{u_{exp}, \omega\})$ is the likelihood function and $p(s, u_{mod})$ is the prior pdf.

In the hypothesis where the difference between observation and corrected frequency is expected to arise from a normal distribution

$$\nu_{exp,i} - s\omega_i \sim N(0, u_{mod}^2 + u_{exp,i}^2), \quad (A3)$$

the likelihood function for a single observed frequency is

$$p(\nu_{exp,i} | s, u_{mod}, u_{exp,i}, \omega_i) = (2\pi (u_{mod}^2 + u_{exp,i}^2))^{-1/2} \exp\left(-\frac{1}{2} \frac{(\nu_{exp,i} - s\omega_i)^2}{u_{mod}^2 + u_{exp,i}^2}\right). \quad (A4)$$

Considering that all frequencies are measured independently (with uncorrelated uncertainty) the joint likelihood is the product of the individual ones, *i.e.*

$$p(\{\nu_{exp}\} | s, u_{mod}, \{u_{exp}, \omega\}) = \prod_{i=1}^N (2\pi (u_{mod}^2 + u_{exp,i}^2))^{-1/2} \times \exp\left(-\frac{1}{2} \sum_{i=1}^N \frac{(\nu_{exp,i} - s\omega_i)^2}{u_{mod}^2 + u_{exp,i}^2}\right). \quad (A5)$$

As there is a priori no correlation between s and u_{mod} , we use a factorized prior pdf $p(s, u_{mod}) = p(s)p(u_{mod})$. In the absence of a priori quantified information on s , a uniform pdf $p(s) = cte$ is used. For u_{mod} , we enforce a positivity constraint through a Jeffrey's prior, $p(u_{mod}) \propto u_{mod}^{-1}$.³³ The posterior pdf is finally defined up to a norm factor which is irrelevant for the following developments

$$p(s, u_{mod} | \{\nu_{exp}, \omega, u_{exp}\}) \propto u_{mod}^{-1} \prod_{i=1}^N (u_{mod}^2 + u_{exp,i}^2)^{-1/2} \times \exp \left(-\frac{1}{2} \sum_{i=1}^N \frac{(\nu_{exp,i} - s\omega_i)^2}{u_{mod}^2 + u_{exp,i}^2} \right). \quad (\text{A6})$$

2. Case of negligible measurement uncertainties

For the analysis of vibrational frequencies, it is generally considered that experimental uncertainties are negligible when compared to model inadequacy ($u_{exp,i} \ll u_{mod}$). The general expression for the posterior pdf (Eq. A6) can then be simplified accordingly:

$$p(s, u_{mod} | \{\nu_{exp}, \omega\}) \propto u_{mod}^{-N-1} \exp \left(-\frac{1}{2u_{mod}^2} \sum_{i=1}^N (\nu_{exp,i} - s\omega_i)^2 \right). \quad (\text{A7})$$

Using Eq. 2 and 3 we derive the identity (see *e.g.* Ref.³³ (, Eq. 9.4, p. 214))

$$\sum_{i=1}^N (\nu_{exp,i} - s\omega_i)^2 = (s - \hat{s})^2 \sum \omega_i^2 + N\gamma^2, \quad (\text{A8})$$

which enables to write the posterior pdf in a convenient factorized form

$$p(s, u_{mod} | \{\nu_{exp}, \omega\}) \propto u_{mod}^{-N-1} \exp \left(-\frac{N\gamma^2}{2u_{mod}^2} \right) \exp \left(-\frac{(s - \hat{s})^2 \sum \omega_i^2}{2u_{mod}^2} \right) \quad (\text{A9})$$

from which we can derive analytical estimates for the parameters and their uncertainties.

a. *Estimation of s*

The marginal density for s is obtained by integration over u_{mod}

$$p(s | \{\nu_{exp}, \omega\}) = \int_0^\infty du_{mod} p(s, u_{mod} | \{\nu_{exp}, \omega\}) \quad (A10)$$

$$\propto \int_0^\infty du_{mod} u_{mod}^{-N-1} \exp\left(-\frac{1}{2u_{mod}^2} \sum_{i=1}^N (\nu_{exp,i} - s\omega_i)^2\right) \quad (A11)$$

$$\propto \left(\sum_{i=1}^N (\nu_{exp,i} - s\omega_i)^2 \right)^{-N/2}, \quad (A12)$$

which, using Eq. A8, can be rewritten as

$$p(s | \{\nu_{exp}, \omega\}) \propto \left(1 + \frac{(s - \hat{s})^2 \sum \omega_i^2}{N\gamma^2} \right)^{-N/2}, \quad (A13)$$

and has the shape of a Student's distribution⁴⁴

$$\text{Stt}(x) \propto \left(1 + \frac{x^2}{n} \right)^{-(n+1)/2}. \quad (A14)$$

Posing $n = N - 1$ and $x^2 = (N - 1)/N (s - \hat{s})^2 \sum \omega_i^2 / \gamma^2$, we can directly use the properties of the Student's distribution

$$\text{E}[x] = 0; \text{Var}[x] = n/(n - 2), \quad (A15)$$

to derive

$$\text{E}[s] \equiv \bar{s} = \hat{s} \quad (A16)$$

$$\text{Var}[s] \equiv u_s^2 = \gamma^2 \frac{N}{(N - 1) \sum \omega_i^2} \text{Var}[x] \quad (A17)$$

$$= \gamma^2 \frac{N}{(N - 3) \sum \omega_i^2} \quad (A18)$$

b. Estimation of u_{mod}

The marginal density for the standard uncertainty of the stochastic variable ϵ_{mod} is

$$p(u_{mod} | \{\nu_{exp}, \omega\}) = \int_{-\infty}^\infty ds p(s, u_{mod} | \{\nu_{exp}, \omega\}) \quad (A19)$$

$$\propto \frac{1}{u_{mod}^{N+1}} \exp\left(-\frac{N\gamma^2}{2u_{mod}^2}\right) \int_{-\infty}^\infty ds \exp\left(-\frac{(s - \hat{s})^2 \sum \omega_i^2}{2u_{mod}^2}\right) \quad (A20)$$

$$\propto \frac{1}{u_{mod}^N} \exp\left(-\frac{N\gamma^2}{2u_{mod}^2}\right). \quad (A21)$$

Using the formula

$$\int_0^\infty dx x^{-n} e^{-a/x^2} = \frac{1}{2} \Gamma\left(\frac{n-1}{2}\right) / a^{(n-1)/2} \quad (\text{A22})$$

to recover the normalization constant of $p(u_{mod} | \{\nu_{exp}, \omega\})$ and to calculate mean values of u_{mod} and u_{mod}^2 , one obtains readily the following estimates

$$\hat{u}_{mod} = \gamma \quad (\text{A23})$$

$$\bar{u}_{mod} = \gamma \sqrt{\frac{N}{2} \frac{\Gamma[(N-2)/2]}{\Gamma[(N-1)/2]}} \quad (\text{A24})$$

$$\overline{u_{mod}^2} = \frac{N}{N-3} \gamma^2 \quad (\text{A25})$$

$$u_{u_{mod}} = \gamma \sqrt{\frac{N}{N-3} - \frac{N}{2} \left(\frac{\Gamma[(N-2)/2]}{\Gamma[(N-1)/2]} \right)^2} \quad (\text{A26})$$

3. Prediction and uncertainty propagation

In the Bayesian framework, the posterior pdf $p(s, u_{mod} | \{\nu_{exp}, u_{exp}, \omega\})$ can be used to estimate the uncertainty of predicted frequencies by the law of propagation of distribution³⁴

$$p(\nu' | \omega', \{\nu_{exp}, u_{exp}, \omega\}) = \int ds du_{mod} p(\nu' | s, u_{mod}, \omega') p(s, u_{mod} | \{\nu_{exp}, u_{exp}, \omega\}), \quad (\text{A27})$$

where

$$p(\nu' | s, u_{mod}, \omega') \propto u_{mod}^{-1} \exp\left(-\frac{(\nu' - s\omega')^2}{2u_{mod}^2}\right) \quad (\text{A28})$$

translates the stochastic prediction model (Eq. 8) as a pdf. This integral has generally to be evaluated numerically.

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